High temperature growth of highly crystalline carbon nanotube from carbon nano-onion seed using ethylene as carbon feedstock

Osaka Univ. [1], Nippon Kayaku [2], °M. Wang[1], K. Nakamura[1], M. Arifuku[2], N. Kiyoyanagi[2], Y. Kobayashi[1]

E-mail: wang.my@ap.eng.osaka-u.ac.jp

[Introduction] High-temperature process in chemical vapor deposition (CVD) is a promising approach to form high quality carbon nanotube (CNT) with fewer defects, and it provides us a new way to improve CNTs' properties in various applications [1,2]. In our previous study [3], we have got high quality CNTs (top/average I(G)/I(D)~300/52) by CVD at 1000℃ with choosing acetylene (C_2H_2) as carbon source and carbon nano-onion (CNO) as growth seed through two-stage growth. C_2H_2 is a suitable material for the growth at usual CVD temperature. However, pyrolysis temperature for C_2H_2 is relatively low, and several complex reaction path ways should be involved above their pyrolysis temperature [4], resulting in difficult control due to violent behavior at high temperature, such as serious deposition of amorphous carbon (a-C). In this work, we explore to use ethylene (C_2H_4) as alternative carbon feedstock for high temperature growth of CNT instead of C_2H_2, since its pyrosis temperature is higher than C_2H_2 and well-behaved growth manner will be expected.
[Experimental] CNO was formed by heating nanodiamond at 1000℃ in Ar for 1 hour and works as the growth seed in CNT synthesis. First of all, CNT was grown using C_2H_4 at constant temperature (1000℃) to examine growth characteristics at high temperature compared with C_2H_2. Then, we tried to improve growth yield of CNT by using two-stage growth process [3], where the CNT cap structures were formed under relatively concentrated condition of the carbon source at 900℃ as the initial growth stage, and then tubular parts were grown at 1000℃ for 30 min as the second growth stage. In the second stage, the partial pressure of the carbon source was kept low (1 sccm C_2H_4(3%)/Ar + 19 sccm H_2(3%)/Ar) and a small amount of water (100-300ppm) was mixed in some experiments to control the growth driving force. The quality and yield of the grown CNT were characterized by Raman spectra using 633 nm excitation.
[Results] Figure 1 compares the Raman spectra from CNTs grown using C_2H_4 and C_2H_2 at 1000℃. Crystallinity of the grown CNTs evaluated from average I(G)/I(D) ratio was observed to be similar, and growth yield estimated from the observation frequency of G-bands was much higher for C_2H_4 (~80%). This result indicates the potential of C_2H_4 suitable for high temperature process.

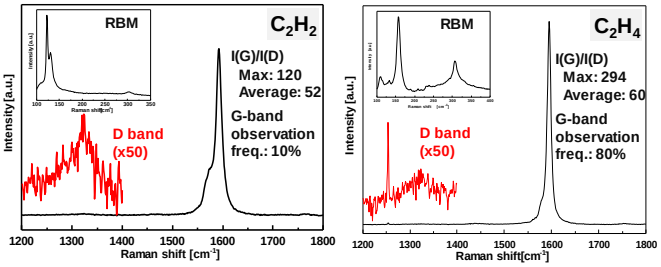

Fig. 1 Raman spectra observed from CNT grown using C_2H_2 (two-stage process with water), and C_2H_4 grown at 1000℃

Figure 2 shows the Raman spectra observed from CNT grown with C_2H_4 as carbon feedstock in two-stage growth process. Just after the initial growth stage at 900℃ (Fig. 2 (a)), the CNTs' growth has been limited in cap structure formation as the preparation for higher CNT yield. While on the temperature increasing process and second stage growth (Fig.2(b), (c)), the partial pressure decreased as described in experimental section. It needs to say that the yield has been obviously improved compared with the yield grown by one stage growth at 1000℃ (Fig. 1). On the other hand, even if water vapor (~200 ppm) has been added on temperature increasing process and subsequent second stage growth to control the driving force and prevent a-C formation, there still got a significant increase of D band intensity in Fig.2(c). The D band must be caused by a-C deposition which was also observed on a blank substrate. Higher concentration of water (>240 ppm) induces defect formation on CNT wall although no a-C is deposited (data not shown). These results indicate that water vapor injected at 1000℃ seems to have complex etching effects severe to control and should etch not only a-C but also CNT structure. More efficient etchant to limit the a-C formation should be explored to achieve the efficient synthesis for very low-defect CNTs.

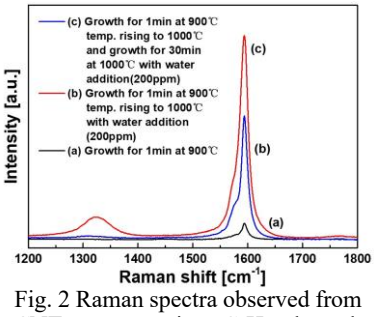

Fig. 2 Raman spectra observed from CNT grown using C_2H_4 through two-stage growth process with water

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